Electronic Supplementary Material (ESI) for CrystEngComm.
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Supporting Information

1. Materials and methods.

Variable temperature single crystal X-ray structure data for the *iso*propanol clathrate of **2** and the *iso*propanol clathrate of the polar *quasi*racemic host **6** were collected on an Agilent Supernova Dual Source, Cu at Zero, Atlas CCD diffractometer equipped with an Oxford Cryosystems Cobra cooling device. The data was collected using mirror monochromated CuKα radiation, (λ = 1.54178Å). Crystal structure data for the *iso*propanol clathrate of **3** was collected on a Siemens SMART IK diffractometer equipped with an Oxford Cryosystems Cryostream cooling device. The data were collected using graphite monochromated MoKα radiation, (λ = 0.71069Å). Structures were typically solved and refined with the SHELX[19] suite of programs. Unless otherwise stated, hydrogen atoms attached to carbon were placed geometrically and allowed to refine with a riding isotropic displacement parameter. Hydrogen atoms attached to a heteroatom were located in a difference Fourier synthesis and were allowed to refine freely with an isotropic displacement parameter. Temperature-dependent crystal structure data for compounds **2, 3** and **6** has been deposited at the CCDC 1400608-1400611, 1400701, and 1400606-1400607 respectively.

Differential scanning calorimetry, (DSC), data were collected on a TA Instruments Q2000 equipped with a 50 position auto-sampler. The calibration for thermal capacity was carried out using sapphire and the calibration for energy and temperature was carried out using certified indium. Typically 0.5 – 3 mg of each sample, in a pin-holed aluminium pan, was heated at 10 °C/min from 25 °C to 300 °C. A purge of dry nitrogen at 50 ml/min was maintained over the sample. The instrument control software was Advantage for Q Series v2.8.0.394 and Thermal Advantage v5.5.3 and the data were analysed using Universal Analysis v4.5A.

2. Residual density discussion

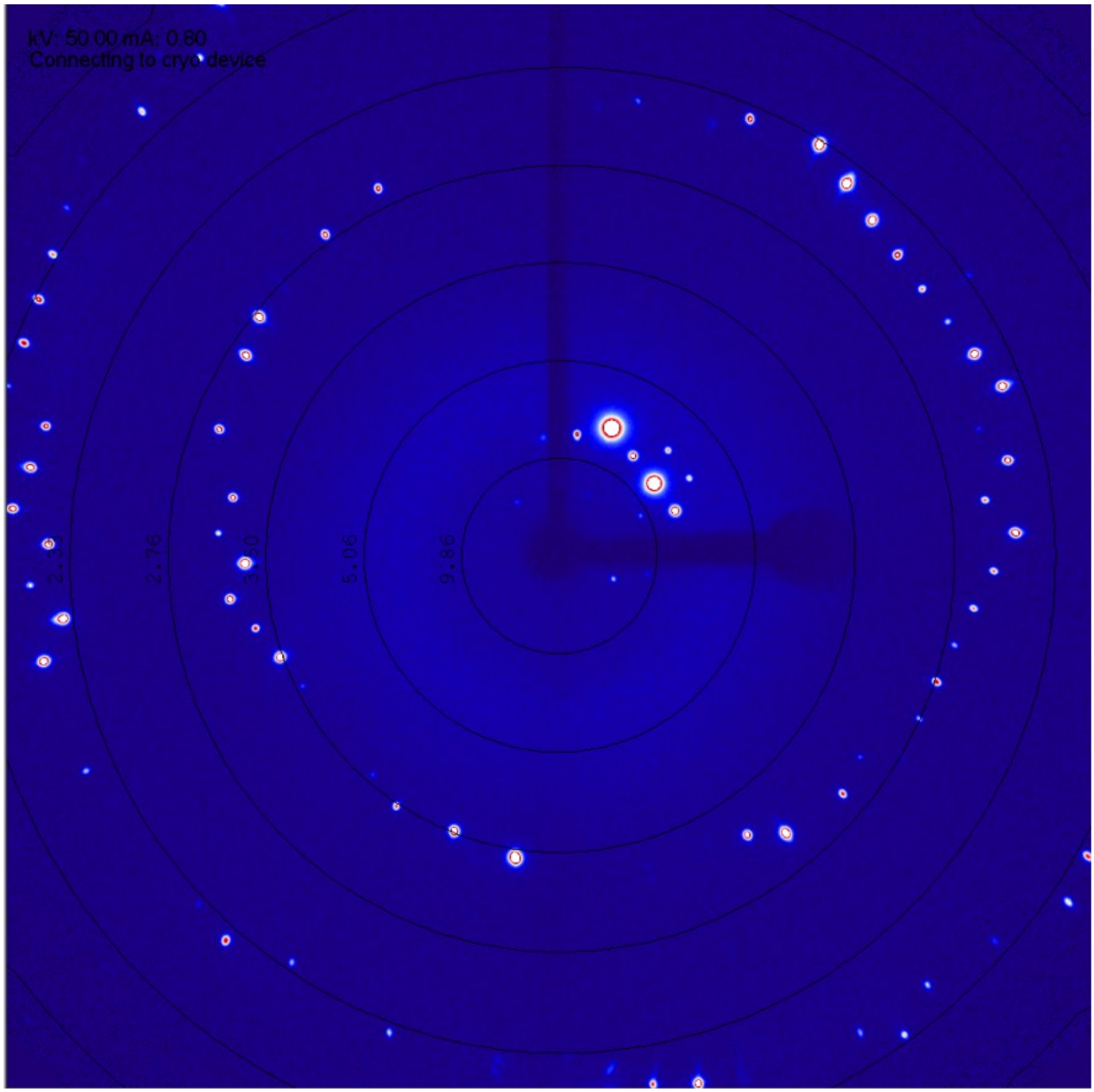
The sixteen independent host molecules in structures **2** (90K) and **3** (120K) are denoted by letters A to P. The six IPA guest molecules are denoted by letters Q to V. The centrosymmetric Type II unit is comprised of host molecules A to C and guest molecule Q. The Type IIIa unit is comprised of host molecules D to I and IPA guest molecules R and S. The Type IIIb unit is comprised of host molecules J to O and IPA guest molecules T and U. The Type I unit is comprised of molecule P and IPA guest molecule V. The IPA guest molecules Q to U are disordered by inversion about a lattice point. The disorder was accounted for by a two-part model. The IPA guest molecule in the Type I unit were statistically disordered about the about the three-fold axis.

The residual density observed in this structure occurs primarily about molecules located in the type II unit, (point of $\bar{1}$ symmetry), the largest peak of which (~2.4 e Å^{-3}) is located 0.93 Å from O1C. There are two other significant peaks in the difference electron density map (1.34 and 1.25 eÅ^{-3}), these are located 0.83Å and 1.05Å from O1A and O1B respectively. Further data sets collected at 90K on different single crystal samples reveal that these peaks in the residual density are reproducible from crystal to crystal possibly indicating a very minor secondary orientation at this temperature, (90 K), for the host molecules located in the type II unit in one step of the evolution of the structure. There is also some abnormality in the temperature factors of the disordered IPA solvent molecules.

3. Diffraction images

Diffraction images taken before and after the low temperature phase transition 200K and 100K, showing the appearance of the new supercell

200K



100K

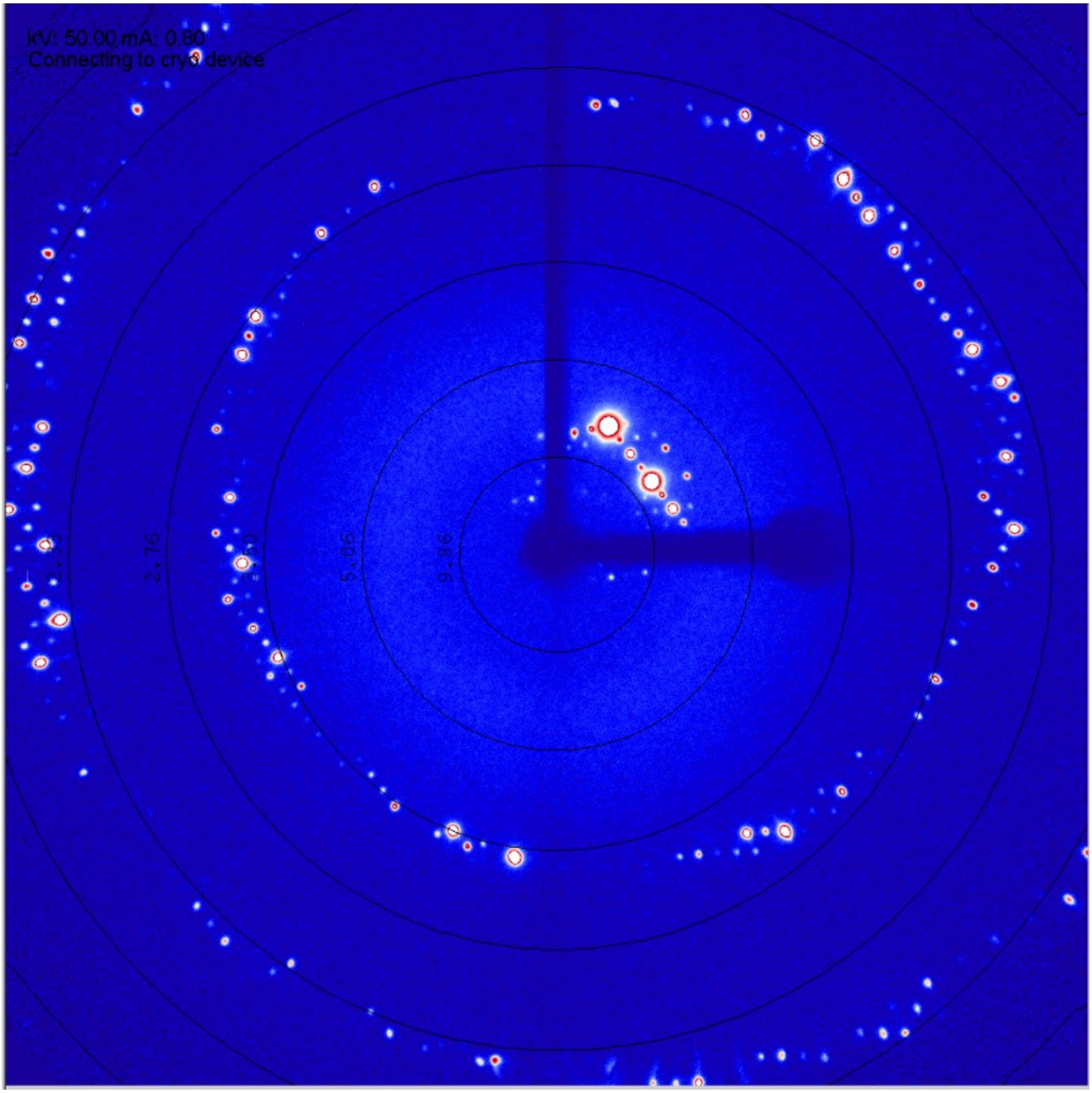


Table S1. Crystallographic data for the temperature dependent structures of the IPA clathrate of **2**.

	2, (371 K)	**2, (295 K)**	**2, (200 K)**	**2, (90 K)**
formula	$C_{18}H_{20}O_1S_1.0.33(C_3H_8O_1)$	$C_{18}H_{20}O_1S_1.0.33(C_3H_8O_1)$	$C_{18}H_{20}O_1S_1.0.33(C_3H_8O_1)$	$C_{18}H_{20}O_1S_1.0.33(C_3H_8O_1)$
crystal system	trigonal	trigonal	trigonal	trigonal
space group	*R*-3	*R*-3	*R*-3	*R*-3
a, (Å)	28.246(4)	56.4934(4)	56.1623(4)	111.7910(5)
b, (Å)	28.246(4)	56.4934(4)	56.1623(4)	111.7910(5)
c, (Å)	10.965(3)	10.9041(1)	10.8866(1)	10.8568(1)
α, (°)	90	90	90	90
β, (°)	90	90	90	90
γ, (°)	120	120	120	120
V, (Å^3)	7576(3)	30138.1(5)	29738.0(6)	117502(1)
Z'	1	4	4	16
Z	18	72	72	288
T, (K)	371(1)	295(1)	200(1)	90(1)
F(000)	2940	11760	11760	47040
D_{calc} (g cm^{-3})	1.201	1.208	1.224	1.239
λ, Resolution (Å)	CuKα, 1.10	CuKα, 0.80	CuKα, 0.80	CuKα, 0.80
μ (mm^{-1})	1.686	1.696	1.719	1.740
crystal size (mm)^3	0.30 x 0.30 x 0.25	0.50 x 0.49 x 0.47	0.55 x 0.53 x 0.53	0.55 x 0.53 x 0.53
Number of reflections	2751	95313	31182	269011
Unique reflections, (R_{int})	1311, 0.1779	13919, 0.0298	13597, 0.0175	53208, 0.0375
wR^2, *all data*	0.4072	0.1614	0.1435	0.1775
R_1, $I > 2\sigma(I)$	0.1493, 711	0.0545, 12538	0.0457, 12305	0.0608 48451
S on F^2	1.981	1.026	1.000	1.048
residual density, (e Å^{-3})	0.496, -0.490	0.924, -0.739	0.554, -0.559	2.299, -0.743
CCDC Deposition Number	1400610	1400608	1400609	1400611

Table S2 Crystallographic data for the temperature dependent structures of the IPA clathrate of **6**.

	6, (290 K)	**6, (90 K)**
formula	$C_{18}H_{20}O_2.C_{18}H_{20}O_1S_1.0.66(C_3H_8O_1)$	$C_{18}H_{20}O_2.C_{18}H_{20}O_1S_1.0.66(C_3H_8O_1)$
crystal system	trigonal	trigonal
space group	$R3$	$R3$
a, (Å)	27.6575(15)	55.0808(9)
b, (Å)	27.6575(15)	55.0808(9)
c, (Å)	10.9557(14)	10.8542(2)
α, (°)	90	90
β, (°)	90	90
γ, (°)	120	120
V, (Å^3)	7257.7	28518.6(11)
Z'	1	4
Z	9	36
T, (K)	290(1)	90(1)
F(000)	2868	11472
D_{calc} (g cm^{-3})	1.221	1.243
λ, Resolution (Å)	CuKα, 0.80	CuKα, 0.80
μ (mm^{-1})	1.182	1.203
crystal size (mm)^3	0.25 x 0.25 x 0.25	0.25 x 0.25 x 0.25
Number of reflections	15972	205222
Unique reflections, (R_{int})	6497, 0.0184	25917 0.0343
wR^2, *all data*	0.1186	0.0815
R_1, $I > 2\sigma(I)$	0.0396, 6267	0.0312, 25644
S on F^2	1.004	1.04
residual density, (e Å^{-3})	0.264, -0.372	0.637, -0.699
Flack Parameter	0.022(5)	0.006(7)
CCDC Deposition number	1400607	1400606

Table S3 Crystallographic data for the 120 K structure of the IPA clathrate of **3**.

	3, (120 K)
formula	$C_{18}H_{20}O_1Se_1.0.33(C_3H_8O_1)$
crystal system	trigonal
space group	*R*-3
a, (Å)	113.983(5)
b, (Å)	113.983(5)
c, (Å)	10.7937(7)
α, (°)	90
β, (°)	90
γ, (°)	120
V, (Å^3)	121445(14)
Z'	16
Z	288
T, (K)	120(1)
F(000)	52224
D_{calc} (g cm^{-3})	1.383
λ, Resolution (Å)	MoKα, 0.80
μ (mm^{-1})	2.226
crystal size (mm)^3	0.45 x 0.45 x 0.40
Number of reflections	410947
Unique reflections, (R_{int})	48884, 0.0875
wR^2, *all data*	0.2577
R_1, $I > 2\sigma(I)$	0.1063, 29779
S on F^2	1.400
residual density, (e Å^{-3})	2.235, -2.822
CCDC Deposition number	1400701

Supplementary Figures

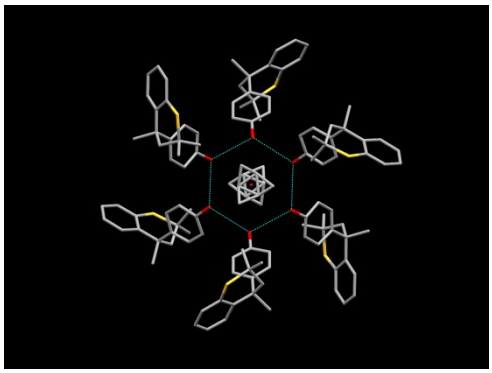


Figure S1

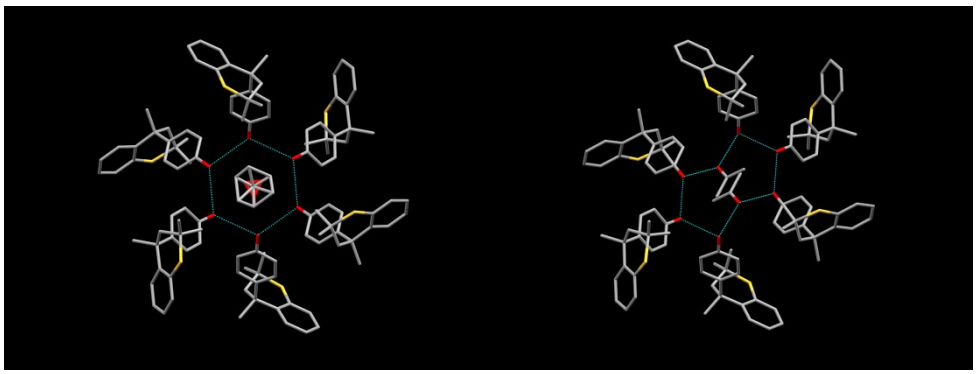


Figure S2a Figure S2b

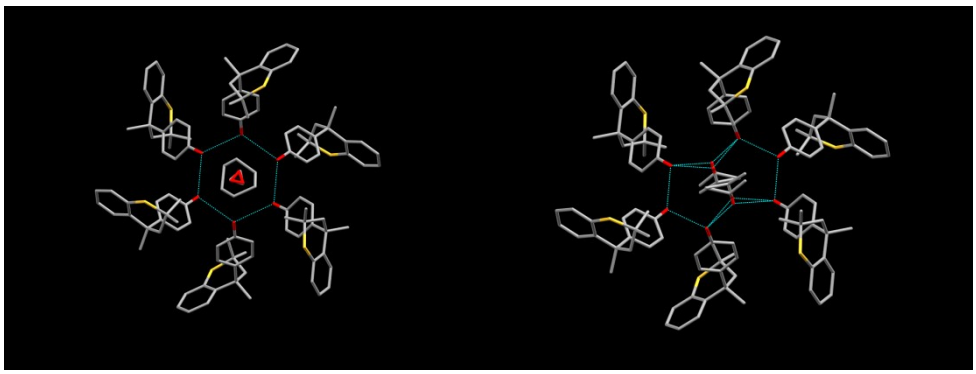


Figure S3a Figure S3b

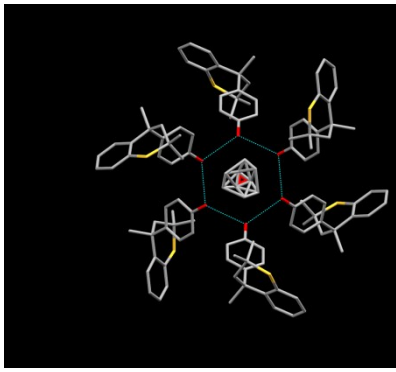


Figure S4a

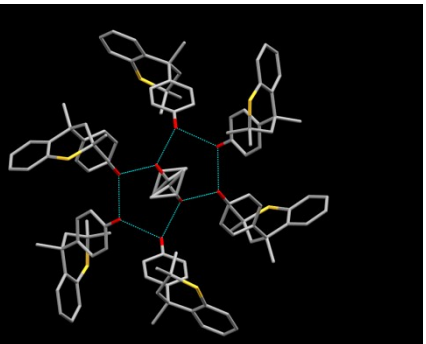


Figure S4b

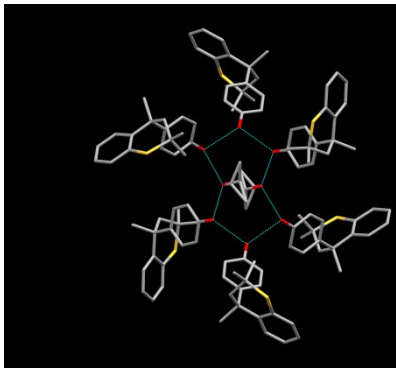


Figure S4c

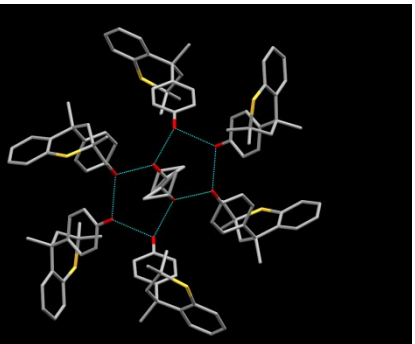


Figure S4d

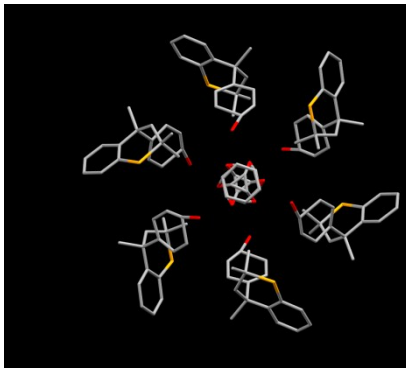


Figure S5a

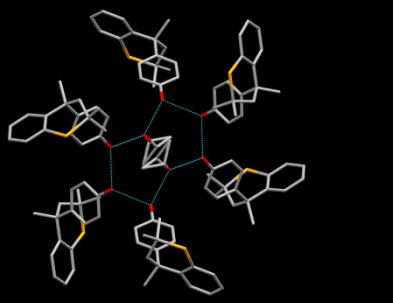


Figure S5b

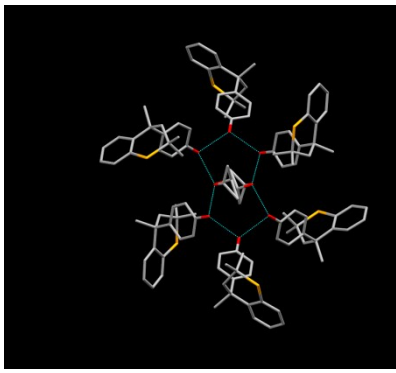


Figure S5c

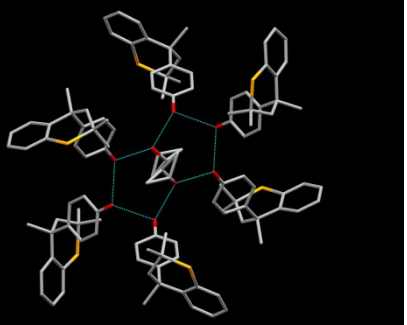


Figure S5d

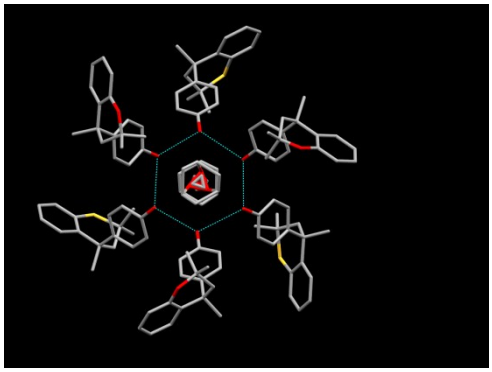


Figure S6

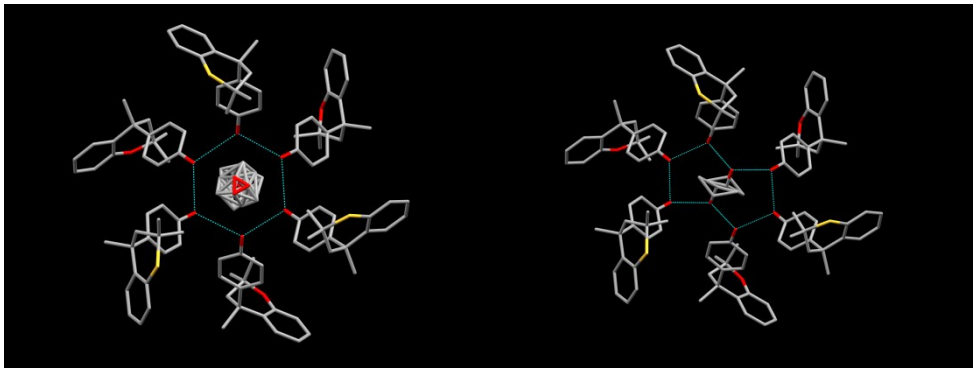


Figure S7a Figure S7b

Supplementary Figure Captions

Figure S1	Type I cage of the *iso*propanol clathrate of **2** at 371 K viewed down the *c*-axis.
Figure S2a	Type I cage of the *iso*propanol clathrate of **2** at 295 K viewed down the *c*-axis.
Figure S2b	Type II cage of the *iso*propanol clathrate of **2** at 295 K viewed down the *c*-axis.
Figure S3a	Type I cage of the *iso*propanol clathrate of **2** at 200 K viewed down the *c*-axis.
Figure S3b	Type II cage of the *iso*propanol clathrate of **2** at 200 K viewed down the *c*-axis.
Figure S4a	Type I cage of the *iso*propanol clathrate of **2** at 90 K viewed down the *c*-axis.
Figure S4b	Type II cage of the *iso*propanol clathrate of **2** at 90 K viewed down the *c*-axis.
Figure S4c	Type III cage, (a), of the *iso*propanol clathrate of **2** at 90 K viewed down the *c*-axis.
Figure S4d	Type III cage, (b), of the *iso*propanol clathrate of **2** at 90 K viewed down the *c*-axis.
Figure S5a	Type I cage of the *iso*propanol clathrate of **3** at 120 K viewed down the *c*-axis.
Figure S5b	Type II cage of the *iso*propanol clathrate of **3** at 120 K viewed down the *c*-axis.
Figure S5c	Type III cage, (a), of the *iso*propanol clathrate of **3** at 120 K viewed down the *c*-axis.
Figure S5d	Type III cage, (b), of the *iso*propanol clathrate of **3** at 120 K viewed down the *c*-axis.
Figure S6	Type I cage of the *iso*propanol clathrate of **6** at 290 K viewed down the *c*-axis.
Figure S7a	Type I cage of the *iso*propanol clathrate of **6** at 90 K viewed down the *c*-axis.
Figure S7b	Type II cage of the *iso*propanol clathrate of **6** at 90 K viewed down the *c*-axis.